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COMBINED APPROXIMATION METHOD FOR ENERGY CALCULATION IN THE MANY-ELECTRON PROBLEM

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COMBINED APPROXIMATION METHOD FOR ENERGY CALCULATION IN /913**
THE MANY-ELECTRON PROBLEM*

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An approximation formula for the quantum-mechanical many-
body problem is developed for the energy calculation of
many-electron configurations, based on utilization of spectro-
scopic data for quantitative chemical analyses. The method
is a combination of the Thomas-Fermi statistical distribution
and the Schrödinger equation, applying the former to the atom
rumpf and the latter to the valence electrons. Application
of the method to the binding energy of K_2 yields only 37% of
the true energy and 39% for KH, with the main reason for the
energy deficiency being neglect of the orbital motion coupling
of electrons due to their interaction. Mathematical develop-
ment of the method is given for the K_2 and the KH molecule as
typical examples.

1. Introduction

It is known that quantum mechanics has been able to "solve in principle"
the chemical fundamental problems. However, despite numerous qualitative re-
sults, an unambiguous quantitative application of the theory, except for a few
limiting cases, to practical chemical problems has never been possible, and the
chemist is usually forced to continue using the old models for obtaining a more
or less quantitative systematics of the great multiplicity of experimental data.
It is by no means a function of theory to recalculate all empirical data indi-
vidually. Nevertheless, one can expect that the theory should furnish a simple,
although rough, theoretical scheme which would interconnect the various proper-
ties of atoms without excessive ambiguity and permit reducing practical problems
of the chemical behavior of atoms to measurable atomic properties of as uni-
versal as possible a character. The present paper is to make some progress in
this direction.

Since, in the final analysis, all properties of a given atom are quantita-
tively reflected in its spectrum, it is logical to attempt using the extensive
spectroscopic material on atoms, for deriving and quantitatively formulating
the chemical properties. We will make an attempt here to develop an approxima-

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tion formula for the quantum-mechanical many-body problem* which is to permit, in a simple manner, the use of spectroscopic data for obtaining quantitative chemical data.

The process consists in a combination of two methods for determining the energy and density distribution in the atom, namely the Thomas-Fermi** statistical distribution and the Schrödinger equation. The rumpf of the atom will /914 be treated according to the Thomas-Fermi method and the valence electrons according to the Schrödinger process. For both together, there exists a variational problem of the form

$$\delta \overline{H} = \delta \overline{U} + \delta \overline{T} = \delta \int (U + T)\, d\tau = 0, \tag{1}$$

where U resp. T denote the potential and the kinetic energy per unit volume, so that H represents the total energy. This energy must be made a minimum which can be done, when using the Thomas-Fermi method, by selecting the total density distribution ρ (Ref.3) and, when using the Schrödinger process, by selecting the eigenfunction ψ. This leads, in the one case, to the Thomas-Fermi differential equation and, in the other case, to the Schrödinger equation.

2. Remarks on Application of the Th-F Theory to Few Electrons

Before further developing the variational problem, it is necessary to settle a few questions with respect to the applicability of the statistical method to only a few electrons. Strictly speaking, the assumptions of this approximation method, namely a large number of electrons in a singled-out partial volume of such a size that the potential is practically constant therein, does not actually exist. Nevertheless, down to a few electrons, more or less useful results are obtained; even for the case of a single electron, the results are still not meaningless. Since it is of importance for our specific purpose to understand the sense and usefulness of the Thomas-Fermi arguments in the presence of a very small number of electrons, we will precede the actual problem by a few general considerations.

First, let us recall that the significance of density distribution ρ in the Thomas-Fermi method differs from that in the Schrödinger process. In the former case, we conceive the individual electrons - although only within the uncertainty produced by their finite space requirement in the phase space - as being localized and, so long as sufficient particles are present, speak of a continuous /915 density function in the conventional thermodynamic sense. This density distribution ρ loses its meaning if only a single particle is present. Let us compare the statements of the two theories for both cases: 1) infinitely many electrons, 2) one electron located in a potential box with impermeable walls. It is known that, in the former limiting cases, the statements coincide for the total kinetic energy of the system, namely

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* The principle of this approximation method was reported previously (Ref.3).

** Below, abbreviated as Th-F.

$$E = T \cdot V = \frac{3h^2}{40m} \left(\frac{3}{\pi}\right)^{2/3} \rho^{5/3} \cdot V, \tag{2}$$

where ρ is the total density of all electrons and V the total volume of the box. In the case of one electron, the wave mechanics, provided that the box - for simplicity - is assumed as rectangular with an edge length a, will furnish the following expression for the total energy in the lowest state:

$$E = \frac{3h^2}{8a^2m}. \tag{3}$$

The corresponding density distribution reads

$$\psi^*\psi = \frac{8}{a^3} \sin^2 \frac{\pi}{a} x \cdot \sin^2 \frac{\pi}{a} y \sin^2 \frac{\pi}{a} z. \tag{4}$$

Recalling the derivation of T(ρ) by means of the Pauli principle, it should be expected that entirely meaningless results are obtained for a single electron. Nevertheless, if the Th–F expression is formally applied to the single electron, the kinetic energy density will be

$$T = \frac{3h^2}{40m} \left(\frac{3}{\pi}\right)^{2/3} \rho^{5/3}. \tag{5}$$

This is not all meaningless for the single electron. To bring eq.(3) into a form corresponding to that of eq.(5), let us introduce, into the wave-mechanical formula, a "mean density per unit volume" $\rho' = 1/a^3$ and a "mean kinetic energy per unit volume" $T' = E/a^3$. Hence

$$T' = \frac{3h^2}{8ma^5} = \frac{3h^2}{8m} \rho'^{5/3} \quad \text{resp.} \quad E = \frac{3h^2}{8m} \rho'^{5/3} \cdot a^3. \tag{6}$$

This makes it possible to compare the two equations (5) and (6), showing /916

primarily that they have the proportionality of T with $\frac{h^2}{m} \rho^{5/3}$ resp. T' with

$\frac{h^2}{m} \rho'^{5/3}$ in common. From this it follows that we must assign to T and ρ in the

Thomas–Fermi method, for the case of a single electron, the significance of a "mean" energy resp. particle density. The quantities ρ'and T', as indicated in eq.(6), by no means agree with the wave-mechanical expressions $\psi^*\psi$ and

$\frac{h^2}{8\pi^2 m} \psi^*\Delta\psi$. Only the total energy T' • V is the same as $-\frac{h^2}{8\pi^2 m} \int\psi^*\Delta\psi d\tau$.

However, quantitatively the value of T' and thus of E, in the strict formula (6), is about five times as high as that obtained by the Thomas–Fermi method. It can be assumed that this error of the statistical method exists also in systems consisting of more than one electron but that it will diminish with increasing number of electrons since, in the limiting case of infinitely many

electrons, both theories coincide. That the Thomas-Fermi method furnishes relatively good results for the total energy in the case of a small number of electrons is due to the fact that the error of too low a kinetic energy is partly compensated by an error in the potential energy which acts in the opposite sense and vanishes similarly with increasing number of electrons.

It is generally known that, in the Th-F theory, the potential energy is expressed not only by the energy of the charge cloud in the external field but also by the total interaction of this cloud with itself. However, in wave mechanics, the sum of interactions of each electron with the contribution to the total charge distribution furnished by this electron itself must be deducted again. This error becomes negligible only in the limiting case of infinitely many electrons. Consequently, in the Thomas-Fermi method one calculates with an everywhere too large potential energy function $U(\rho)$ and an everywhere too small function $T(\rho)$. In both cases, the percentual error becomes greater the less electrons are present. Obviously, the fact that both errors partially compensate each other is responsible for the finding that the Thomas-Fermi arguments are still useful for the energy calculation of systems of relatively few electrons.

3. Substantiation of a Combined Approximation Method /917

We can now start with our actual task, namely that of resolving the general variational problem (1) into two subproblems. The one portion, consisting of a relatively large number of electrons, is assumed to represent completely closed configurations in the sense of statistical theory, i.e., a closed atom rumpf or a sum of such rumpfs that practically do not interact. Let the contribution of this portion to the total density distribution be almost independent of whether the remaining electrons, i.e., the "valence electrons" are present or not. For the valence electrons, into which we include the total charges outside of the closed rumpfs, it is assumed that their density contribution in the region of the rumpfs is small in comparison with the density ρ_0 produced by the rumpf electrons themselves.

Let us assume that the rumpf problem itself is solved. Consequently, we have to do with the density distribution ρ_0 as well as with $U(\rho_0)$ and $T(\rho_0)$ which make the integral $H_0 = \int [U(\rho) + T(\rho)] d\tau$, under the auxiliary condition $\int \rho \, d\tau = N$, a minimum. We now add to this system the relatively low charge Δ_ρ of the valence electrons[*] which are normed to $\int \Delta \rho \, d\tau = n$ and then seek the energy and density distribution of the entire system.

The original density distribution then changes in two different ways. On the one hand by the fact that the density distribution ρ_0 of the rumpfs, under maintenance of the norming, is modified somewhat ("polarization" of the rumpf by the valence electrons). This component is denoted by $\delta\rho_0$, and $\int \delta\rho_0 \, d\tau = 0$ is valid for it. This modified density distribution of the rumpfs is superposed, however, by the additional density Δ_ρ of the valence electrons with $\int \Delta \rho \, d\tau = n$.

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[*] Actually, we only assume smallness of Δ_ρ in the region in which ρ_0 differs from zero, i.e., in the atom rumpfs.

Expanding ρ in Taylor series and making use of the smallness of the density variation ($\delta\rho + \Delta\rho$), the energy of the system with valence electrons will read

$$\bar{H} = \int \left[U(\rho_0) + T(\rho_0) + \left(\frac{\partial U}{\partial \rho_0} + \frac{\partial T}{\partial \rho_0} \right) \delta\rho + \right.$$
$$\left. + \left(\frac{\partial U}{\partial \rho_0} + \frac{\partial T}{\partial \rho_0} \right) \Delta\rho \right] d\tau . \tag{7}$$

Here, the integral over $U(\rho_0) + T(\rho_0)$ is simply the energy H_0 of the rumpfs alone. The integral $\int \left(\frac{\partial U}{\partial \rho_0} + \frac{\partial T}{\partial \rho_0} \right) \delta\rho \, d\tau$ vanishes since ρ_0 has been selected such that this vanishing takes place for each allowed minor variation $\delta\rho$, compatible with the boundary and auxiliary conditions. Accordingly, the vanishing of the integrand takes place only for the neutral atom and then only if strict solutions of the Thomas-Fermi differential equation for ρ_0 are used. For ions, the integrand is a constant ($\neq 0$); see also (Ref.4). If the Th-F solutions are modified by admitting only certain ρ_0 as competition, for example those sufficiently vanishing at infinity (Ref.5), then the integrand will no longer vanish for the neutral atom whereas the entire integral does vanish. The assumption that $\delta\rho$ is sufficiently small for permitting a restriction to the first term of the Taylor expansion is based on general knowledge of the shell structure of atoms. Details of the shell structure, such as the existence of fully closed rumpfs, are not reflected by the Th-F theory. This empirical fact can be introduced as an expansion and improvement of the theory, by assuming that also terms with $(\delta\rho)^2$ are still small in comparison with the higher powers of $\Delta\rho$, which will be taken into consideration below. Terms with $\delta\rho \Delta\rho$, finally, can be conceived as being added in first approximation to the integral $\int \left(\frac{\partial U}{\partial \rho_0} + \frac{\partial T}{\partial \rho_0} \right) \cdot$

$\cdot \Delta\rho \, d\tau$, by assuming slightly modified $\frac{\partial U}{\partial \rho_0}$ and $\frac{\partial T}{\partial \rho_0}$. For the moment, however, we will restrict the calculation to the first term of the series $\Delta\rho$.

In solving the minimum problem for the entire system, at given ρ_0 and after separation of the integral with ρ_0, the minimum requirement for the component of the total energy contributed by the valence electrons will be

$$\bar{H} - \bar{H}_0 = \int \left[\left(\frac{\partial U}{\partial \rho_0} \right) + \left(\frac{\partial T}{\partial \rho_0} \right) \right] \Delta\rho \, d\tau \tag{7a}$$

or, with the known relation

$$\int \frac{\partial U}{\partial \rho_0} \Delta\rho \, d\tau = - \int_{hal} V_0 \Delta\rho \, d$$

where V_0 denotes the entire electrostatic potential field of the rumpfs,

$$\bar{H} - \bar{H}_0 = \int \left(-e\,V_0 + \frac{\partial T}{\partial \rho_0} \right) \Delta\rho\,d\tau.$$

<div align="right">(7b)</div>

If, without consideration of the Pauli principle or of the Fermi statistics, we had added the valence electrons to the rumpfs for the entire system, then only the term with $-eV_0$ would have occurred under the integral. In that case, we would have found that, under the influence of the high positive potential in the rumpf, the valence electrons would have penetrated deeply into the rumpf itself. That these electrons would not have penetrated completely into the nucleus would have been due only – similar to the case of the valence electron of the H atom – by the fact that they themselves possess a finite space requirement in the phase space, i.e., a zero-point energy, even if no further electrons are present. This kinetic energy component, due to the finite momentum width of each valence electron, does not even occur in eq.(7). The component is of a higher order in $\Delta\rho$, namely, proportional to $(\Delta\rho)^{5/3}$*. A term with $(\Delta\rho)^{5/3}$ would be of importance, in first approximation, only if eq.(7) would not contain the

much higher kinetic energy $\left(\dfrac{\partial T}{\partial \rho_0} \right)$. In the Th–F theory, $\dfrac{\partial T}{\partial \rho_0}$ means the maximum

kinetic energy for one electron, occurring in the studied point of space, /920 whereas eq.(7b) states that the added valence electrons must assume exactly this maximum kinetic energy if they are to stay within the already existing density

distribution ρ_0. The auxiliary term $\dfrac{\partial T}{\partial \rho_0}$ to the potential thus is a direct

consequence of the Pauli principle. Our derivation of eq.(7b) shows that the forces, due to the Pauli principle respectively to the zero-point pressure of the rumpf electron cloud, can be approximately considered in the form of an auxiliary potential to the electrostatic potential field in which the valence electrons are located.

In eq.(7b), we also neglected the following:

1) The finite momentum width of the valence electrons themselves since they were singly-unique imparted the maximal momentum P

$$\left(P = \sqrt{2m\,\frac{\partial T}{\partial \rho_0}}, \text{ since } \frac{P^2}{2m} = \frac{\partial T}{\partial \rho_0} \right).$$

2) The electrostatic mutual interaction of the valence electrons which also is of a higher order in $\Delta\rho$

$$\left(\sim \frac{e^2}{2} \int \frac{\Delta\rho\,(1) \cdot \Delta\rho\,(2)}{r_{12}}\,d\tau_1\,d\tau_2 \right).$$

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* We proved above that, for an order-of-magnitude estimate, eq.(2) for T can be used even for a single electron provided that ρ denotes its mean density in the available space.

3) The Pauli principle for the valence electrons in interaction. All these terms are difficult to approximate by statistical means since the nondivisibility of e is important for this and since in the case of too few electrons, we no longer can speak of an electron density in the sense of the Thomas-Fermi theory. These three components of the energy will be formulated from the wave-mechanics viewpoint; however, it will be stipulated that the entire interaction of the valence electrons with the rumpfs can be approximately described by the potential

field $-eV_0 + \dfrac{\partial T}{\partial \rho_0}$.

Even if we retain eq.(7b) as well as the semi-classical concept of the electron as being a particle localized within the atom, eq.(7b) will already yield statements going beyond the statements of the Thomas-Fermi theory for an atom with valence electrons.

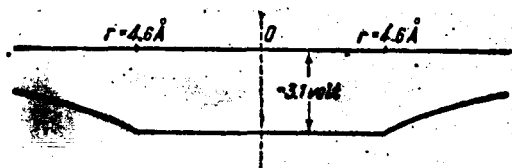For example, let us apply eq.(7b) to the valence electron of an alkali atom. According to eq.(7b) and to the known Thomas-Fermi solutions for an ion (Ref.4), the rumpf field into which the valence electron penetrates has the following consistency: On the outside, up to a radius r_0 which is about 4.6 Å for monovalent ions (Ref.4), the Coulomb

Fig.1

field $\dfrac{e}{r}$ prevails. Starting from r =

= r_0, the entire field $V_0 - \dfrac{1}{e}\dfrac{\partial T}{\partial \rho_0}$

remains constant and equal to the potential $V_0 = \dfrac{e}{r_0}$ at the boundary of the

ion. Figure 1 shows the slope of the potential function for the valence electron. Obviously, in eq.(7b) minimal energy is obtained if the charge of the valence electron is brought to the bottom of the potential box sketched in Fig.1. It is also obvious – going beyond the approximation of eq.(7b) – that the momentum width of the valence electron will be extremely narrow since the available space is extremely large, meaning that neglecting a term of the order of magnitude $\sim(\Delta\rho)^{5/3}$ in the energy is entirely justified. Similarly, an elimina-

tion of $\dfrac{e^2}{2}\int\dfrac{\Delta\rho(1)\cdot\Delta\rho(2)}{r_{12}}d\tau_2 d\tau_1$ is not only justified but even necessary

for improving the Thomas-Fermi formula, since the individual electron has no interaction with itself. Consequently, the ionization energy of the valence

electron, using our approximation, will be obtained as $V_0 = \dfrac{e^2}{r_0}$. This comes

to 3.1 v, which applies universally to all alkali atoms. In the case of cesium, where the prerequisites for application of the Th-F differential equation to the rumpf, i.e., of the potential field shown in Fig.1, are most likely to exist, the real ionization energy is 3.9 v, i.e., still in fair agreement.

We now will go beyond the Thomas-Fermi theory by adding the originally neglected terms of higher order, that do not explicitly depend on the charge dis-

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tribution of the rumpfs, to eq.(7b) in the Schrödinger form[*]:

$$\overline{H} - \overline{H}_0 = \int \left(-eV_0 + \frac{\partial T}{\partial \rho_0} \right) \Delta\rho\, d\tau +$$

$$\int U'\psi^*\psi\, d\tau_1 d\tau_2 \ldots - \frac{h^2}{8\pi^2 m} \int \psi^* \sum_i \Delta_i \psi\, d\tau_1 d\tau_2 \ldots ,$$

(8a)

where ψ depends on the coordinates of all valence electrons while U' is their interaction as a function of the configuration[**]. If the expression in parentheses under the first integral is denoted by V', we can write

$$\int V'\Delta\rho\, d\tau = \int \sum_i V_i' \psi^*\psi\, d\tau_1 d\tau_2 \ldots ,$$

(8b)

where the subscript i means that the total potential function V' must be written successively in the coordinates of each electron. This finally yields a variational problem for the valence electrons which differs from the conventional type only by the fact that, in addition to the electrostatic field of the rumpf

electrons, a counteracting "auxiliary field" $\dfrac{\partial T}{\partial \rho_0}$ occurs which no longer is of

electrostatic origin but is defined by the electron configuration in the rumpf alone.

4. Discussion of the Modified Schrödinger Equation

Our Schrödinger equation for the valence electrons thus has the normal form

$$\left[\sum_i -\frac{h^2}{8\pi^2 m} \Delta_i + U(1 \cdot 2 \ldots) \right] \psi = E\psi,$$

(9)

except for the fact that U contains the auxiliary potential: $U = -eV_0 + \dfrac{\partial T}{\partial \rho_0} +$

+ U'. If ψ is made antisymmetric in the coordinates of the valence electrons, /923 the Pauli principle of these electrons is satisfied. Conversely, no additional stipulation with respect to the quantum states of the rumpf will occur: The exclusion principle, which otherwise forces the electrons into external orbits, has been replaced here by a force that pushes the electrons toward the outside. Whereas an exclusion principle – without antisymmetrization of the total function respectively without inclusion of all individual functions of the rumpf electrons into the perturbation problem – can be formulated only for the quantum states of

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[*] This is no formally consequent continuation of the above-started series expansion of the Th-F problem.

[**] This also corrects the interaction of the electrons with themselves which had been wrong in the Thomas-Fermi theory.

one valence electron relative to the corresponding rumpf and then only in first approximation*, the auxiliary potential of each rumpf will affect all valence electrons of the entire system. As demonstrated on typical examples below, this fact is extremely important and results in distinct improvements over treatments of the binding problem that do not at all consider the rumpf itself or only take its electrostatic effect into consideration and that allow for the Pauli principle in the form of an "occupation rule".

A loose analog to this - at first glance rather surprising - replacement of a quantum rule by introduction of some force is, for example, the fact that, in the H atom, the kinetic energy produced by the rotational motion, exactly

like an auxiliary potential energy $+ \dfrac{h^2}{8\pi^2 m} \dfrac{\iota(\iota + 1)}{r^2}$, enters the differential

equation for the r-dependent component of the eigenfunction. Here, the quantization of the angular momentum forcedly leads to an increase in kinetic energy as soon as the electron approaches the nucleus.

For the moment, the entire theory developed here must be considered as a tentative method, possibly in the same sense as the Thomas-Fermi method itself, whose practical applicability to atoms cannot be theoretically fully substantiated. Nevertheless, practical success of the Th-F method has been recorded. <u>1924</u> However, since we are attempting a considerable improvement of the accuracy obtainable by the Th-F process, our method can be evaluated only on the basis of the obtained results. We will do this in Sections 6 and 7, after introducing an important quantitative refinement in Section 5, based on spectroscopical empirical data. At this point, however, we can already give a few general data as to the statements of our modified Schrödinger equation for valence electrons.

A serious difficulty in the practical application of the arguments to any atoms is presented by the fact that the basic term of our modified Schrödinger equation, because of the spherical symmetry of the potential, always will be an s term. Consequently, all electrons of an atom outside of completely closed shells must be considered "valence electrons" in the sense of our arguments. Despite the fact that an expansion in $\Delta\rho$ is justified if the total number of valence electrons is no longer small, so long as the contribution of these valence electrons to the density in the rumpf region remains low, a practical calculation of binding problems is still impossible if too many "valence electrons" are present. However, it is not the purpose of these rough statistical arguments for the influence of the rumpf on the valence electrons to give all fine details of the spectrum produced by the influence of the incomplete shells

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* The Pauli principle is exactly satisfied only in Fock's treatment of the many-electron problem. By adding the Fock exchange terms to the Hartree equations, the orthogonality of the system of eigenfunctions, which had been lost in Hartree's method, is restored if the difference of the shielding field for the various electrons is taken into account. It must be considered that the Pauli principle requires more than just the exclusion of multiple occupation of identical eigenfunctions; in fact, the principle stipulates the occupation of "different" eigenfunctions which means, as also indicated by Fock's theory (Ref.6), of orthogonal eigenfunctions.

on the optical electron. The true field of application of this approximation method is that of chemical problems, in which it is only a question of defining the rumpf effect more accurately than can be done by the exclusion principle alone, under neglect of all interactions with the rumpf.

In the first two groups of the periodic table, the above arguments are quite useful, in that always only one or two electrons are treated as valence electrons[*].

Above, we considered the cesium valence electron in a semiclassical manner, according to the modified Thomas-Fermi theory. Very little is changed in the energy by using the corresponding Schrödinger equation for Fig.1. Without actual calculation, it can be predicted that, in view of the size of the potential box, the basic term in this field will be located only slightly above the bottom of the box. Considering that the valence electron without auxiliary potential – and without applicability of the exclusion principle – in the electrostatic field of the rumpf would almost fall into the K shell and during this process take on an ionization energy of many thousands of volts, an agreement with the measured ionization energy to within about 1 v must be considered an entirely satisfactory proof for the basic justification of introducing our auxiliary potential. However, for practical purposes this accuracy is insufficient; in Section 5, we will give further refinements which are extremely small

in comparison with the total effect of the auxiliary potential $\dfrac{\partial T}{\partial p_0}$ although,

in order of magnitude, they do attain the binding energies calculated with such atom models.

Let us first discuss another possible objection. Should one not expect that our valence function, at least in its general character, would coincide with the eigenfunction obtained from the Hartree method under application of the exclusion principle? However, this will never be the case, even if the slope of the auxiliary potential, used in the example of cesium, is refined further. This is so since our function, as basic function in the potential field, for example will never show the nodes of the Hartree function[**].

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[*] To obtain a simpler formalism for more complex atoms, in which incomplete inner shells play a role for their chemical behavior, it might be possible to include, in the auxiliary potential, terms that depend on the square of the angular momentum (as operator), so as to allow for the fact that the resistance offered by a rumpf with incomplete shells to the penetration of a valence electron will depend not only on the local coordinates of this electron but also on the square of its angular momentum (i.e., on the momentum quantum number in the case of the valence electron of the free atom). Conversely, such incomplete shells can be included into the rumpf. Occasionally, it may be permissible to retain the exclusion principle in part. We hope to return later to this particular question.

[**] The well-known Slater rule for obtaining nodeless eigenfunctions for the electrons of an atom can be interpreted in the sense of the combined approximation method. Here, each electron, as eigenfunction and eigenvalue,   (cont'd)

A comparison of the expressions for the basic term of the valence electron, formed either with the Hartree solution or with our own solution and the per- taining Hamilton functions, indicates clearly that the two quantities ψ cannot be equal since the two Hamilton functions differ greatly from each other while the ionization energies must be equal. According to Hartree-Fock, the exclusion principle which stipulates that a certain excited eigenfunction must be used for ψ, results in the fact that the integral contribution of the field with high negative values of H remains negligible since $\psi^*\psi$, even in this region, has small values everywhere. In our case, H is either not negative at all or only faintly so in the vicinity of the nucleus; for this reason, our valence electron does not have too low an energy. At a greater distance from the atom rumpf, the slope of the two eigenfunctions presumably will be similar since, in both cases, a practically pure Coulomb field is involved. For the same reason, the higher excited states of the valence electron and the pertaining eigenfunctions will not differ excessively in either case.

For all energy problems into which the eigenfunction of the electrons enter, this has no absolute significance independent of the corresponding rumpf. In using Hartree solutions, so long as one does not change to the many-electron problem, the existence of states occupied by rumpf electrons must always be allowed for by auxiliary rules. The treatment of a valence electron as a truly excited electron with unoccupied ground states almost always leads to errors since, in any perturbation, a portion of the total charge will enter this un- occupied space of high negative potential and thus greatly reduce the energy. In reality, the rumpf electrons block the access of further charge components. In our case, this is expressed in the auxiliary potential which, in contrast to the exclusion principle, affects each charge component no matter where it origi- nates. Conversely, the exclusion principle does not prevent, for example, the charge cloud belonging to a second atom from partly penetrating into the rumpf of the first atom. Similar errors are committed if the polarization energy of a valence electron in the external field is calculated in the same manner as that of an excited atom with unoccupied inner shells. Despite the exclusion principle for the valence electron itself, we definitely obtain excessive polari- zation energies since the formal perturbation calculation always leads to a strong participation of the – in reality forbidden – rumpf states of high nega- tive potential energy in the perturbed eigenfunction

It is obvious that the eigenfunction of the valence electron, according to Hartree, has no significance independent of the quantum states of the rumpf, i.e., that, according to Hartree, no closed one-electron problem is involved here.

In a comparison of the total charge distribution of the atom, obtained by calculating the contribution of valence electrons according to Hartree and by

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* (cont'd) is given the fundamental solution in the field $-\dfrac{e^{27}}{r} +$

$+ \dfrac{h^2}{8\pi^2 m} \dfrac{n^*(n^* - 1)}{r^2}$ where z and n^* are determined by the electrostatic effect of the deeper lying charges, by the Pauli principle, and by the quantum statis- tics for the angular momentum.

using our approximation solutions for the valence electrons, it must be considered that, in both cases, one starts from the variational problem, meaning that the density distribution may show distinct deviations from the real distribution no matter how accurate the calculated energies might be.

As criteria for the usefulness of one or the other description of valence electrons, the only possibility is to calculate practical examples. James (Ref.7) demonstrated recently that all investigations, in which satisfactory results for the binding energy of two atoms were obtained exclusively from the eigenfunctions of the valence electrons, are based on ad hoc assumptions and give an entirely erroneous picture of the real conditions. This is so since, on neglecting the repulsion of all stray valence electrons with the rumpfs, the energy decreases excessively which makes it appear - for example - as though practically no polarization forces participated in the binding (for an extensive literature, see James loc. cit.). In part, exactly as expected, the binding energy - already in first approximation, i.e., without polarization forces - will be considerably higher than the experimental value (Ref.8). We will return to these problems in Section 6, when comparing our results with those correctly calculated by James (Ref.7) on the basis of the many-electron problem.

5. Semiempirical Method

The above-mentioned example of the atom with one valence electron shows that correction of the Schrödinger equation according to the Thomas-Fermi method, /928 in comparison with the corrected effect which approximately corresponds to the ionization energy of an electron in the K shell, is quite satisfactory but not sufficient for calculating terms of the valence electron or binding energies of two atoms. However, after demonstrating the basic justification of the auxiliary potential, there is no objection to using an empirical modified value for

$-eV_0 + \dfrac{\partial T}{\partial \rho_0}$, so far as feasible. In that case, higher-order terms such as

polarization forces between valence electrons and rumpf are partly included. As an extensive and accurate empirical data complex, we have the spectra of the atoms at our disposal. The task consists in finding, from the known terms, a potential field and an eigenfunction system in which the ground state of the valence electron appears as the absolutely lowest state.

Along general lines, the form of our potential can already be predicted. At great distances from the rumpf, we have - except for small polarization corrections which will be disregarded here - a pure Coulomb field. The terms $-eV_0$

and $\dfrac{\partial T}{\partial \rho_0}$ produced by the rumpf both will decrease toward the outside, approxi-

mately as the density of the rumpf electrons, i.e., about exponentially and by one order of magnitude more rapidly than the density of the valence electrons themselves. At the interior of the rumpf, we will at first disregard any finer structure of the total potential. This can be done since we are restricted anyway to approximation arguments which, in the spectroscopic sense, are extremely rough. It must be made clear that we cannot have the goal of reproducing the spectrum of an atom with even halfway spectroscopic accuracy; in the subsequent

application to chemical binding problems, the requirements as to accuracy are much more modest.

Consequently, we will construct the total potential from the Coulomb function and from an exponentially rapidly descending function. For the latter, the type $A \cdot \dfrac{1}{r} e^{-2\varkappa r}$, among all calculated examples, seemed most suitable. Here, $1/\varkappa$ had about the value of half the orbital radius of the valence electrons and A was larger than 1, so that the occurrence of a second potential well at $r =$

$$= 0 \text{ in } -eV_0 + \frac{\partial T}{\partial \rho_0} = -\frac{1}{r} + \frac{A^{-2\varkappa r}}{r}$$ was prevented. An argument $A/r^2 \cdot e^{-2\varkappa r}$ /929

would avoid this in any case; for purely external reasons, namely because of the fact that the exchange integrals later occurring in the binding problem are somewhat more convenient, we retained the first argument.

It would be easy to determine the constants in the potential formula and the eigenfunctions from the spectra, if there would exist strict solutions of the Schrödinger equation for this potential. However, this is not the case. Therefore, we are forced to use the Ritz method for obtaining approximation solutions. At known A and $\varkappa$, the minimum requirements would determine all parameters of the eigenfunctions. To define A and $\varkappa$, the known term value of the basic term and that of the lowest p-term are used. The rapid drop of our auxiliary potential finally causes the spectrum to become hydrogen-like for the more excited terms.

On introducing this potential and these eigenfunctions into some perturbation problem, the Ritz method can be used without restriction. However, since we adjusted A and $\varkappa$ such that the basic term of the free atom is obtained correctly with only approximate eigenfunctions, the auxiliary potential no doubt will be somewhat too low. This does not matter since the "slightly incorrect" eigenfunctions will be retained in each of the subsequent perturbation calculations.

On application of the Ritz method, one can introduce an arbitrary number of parameters into the actual perturbation calculation; because of the requirement that A and $\varkappa$ must be so selected that, at vanishing perturbation energy, the lowest atom terms are correct, one has the assurance that, for each approximation degree of the eigenfunction, the energy of the free atom - for example, due to the variational parameters of the perturbation problem - will not drop below the true basic term.

Finally, we should mention again that the mutual interaction of the rumpfs is not contained in the previous formulation of the theory. It can be stated only that this interaction presumably will be of the next higher order relative to the interaction of the valence electrons with the rumpfs of the other atom. To take this approximately into consideration, the density distribution ρ_0 /930 of the rumpfs should be known. However, as interaction, it is not permitted to use the potential energy of the density of the one atom in the total field

$-eV_0 + \dfrac{\partial T}{\partial \rho_0}$ of the other atom. Since this field does not have an electrostatic

origin, the formula energy = "potential" × charge is applicable only for charges that are small in comparison with the charge ρ_0. However, this is no longer the case when the two rumpfs overlap; rather, there now exist regions in which the charge of the one atom is high and regions in which that of the other atom is high as well as regions in which both are equally large. For calculating the interaction of the two rumpfs as a consequence of the Pauli principle we must return here to the consequent expression (Ref.5)

$$\Delta T = \frac{3h^2}{40m}\left(\frac{3}{\pi}\right)^{2/3}\int[(\rho_a + \rho_b)^{5/3} - \rho_a^{5/3} - \rho_b^{5/3}]\,d\tau \tag{10}$$

which is transformed into $\int \frac{\partial T}{\partial \rho_a}\,\rho_b\,d\tau$ only if everywhere $\rho_b \ll \rho_a$. This would

be supplemented by the regular electrostatic interaction of the rumpfs. For the moment, this portion of the total interaction of the two atoms will be completely disregarded.

The approximation arguments described in this Section can be extended further. However, they are completely sufficient for obtaining valuable orienting results for simple binding problems. As a typical example, we selected the K atom and its compounds K_2 and KH.

6. The K_2 Molecule

Let us check the usefulness of our arguments on the example of the K_2 molecule. The potential formula had been discussed above. As eigenfunction for the valence electron, only the type $r\psi = r^\beta e^{-\epsilon r}$ is actually in question.

This furnishes, in atomic units, the mean kinetic energy in a state with the angular momentum l:

$$\overline{T} = \frac{\epsilon^2}{2\beta - 1}\left(\frac{1}{2} + \frac{l(l+1)}{\beta}\right).$$

The mean potential energy is

$$\overline{U} = \frac{\epsilon}{\beta}\left(-1 + A\left(\frac{\epsilon}{\epsilon + \varkappa}\right)^{2\beta}\right)$$

where β and ϵ represent variational parameters whose selection (at given A and $\varkappa$) makes H = T + U a minimum. For practical reasons, however, we will admit only integral values for β. In the case in question, $\beta = 1$ is the suitable selection, meaning that we are using hydrogen-like functions for the valence electron of K.

The ground state then furnishes two equations $\overline{H} = E$ and $\frac{\partial\overline{H}}{\partial\epsilon} = 0$ for the

three unknowns ϵ, A, $\varkappa$. Instead of using the first excited state with $l = 1$, we used our orienting calculations $\varkappa = 2 \cdot \epsilon_0$ (here ϵ_0 makes $\overline{H}$ a minimum), for

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simplicity. The estimate is reasonable since, as shown above, $\dfrac{A}{r} e^{-2\varkappa r}$ must

decrease by one order of magnitude more rapidly than $\rho = \dfrac{\epsilon^3}{\pi} e^{-2\epsilon r}$. Thus,

already the known term value $E = -0.1596$ of the ground state yields $\epsilon = 0.29$; $\varkappa = 0.58$; $A = 2.743$. For the lowest p term and using our $\varkappa$ value, the energy will be by 5% too low; for this reason, $\varkappa$ and A should really be selected somewhat smaller. However, for a first orientation we will retain the original estimate.

In the K_2 problem, the perturbation energy in the singlet state will read

$$W = W_0 + \frac{2A}{1+s^2}\left(\int \frac{1}{r_b} e^{-2\varkappa r_b} \psi_a{}^2 d\tau + s \int \frac{1}{r_b} e^{-2\varkappa r_b} \psi_a\psi_b d\tau \right) +$$

$$+ \frac{2s}{1+s^2}\left[(\epsilon - 1)\left(\int \frac{1}{r_a} \psi_a\psi_b d\tau - s \int \frac{1}{r_a} \psi_a{}^2 d\tau \right) + \right.$$

$$\left. + A\left(\int \frac{1}{r_b} e^{-2\varkappa r_b} \psi_a\psi_b d\tau - s \int \frac{1}{r_b} e^{-2\varkappa r_b} \psi_b{}^2 d\tau \right) \right]$$

$$s = \int \psi_a\psi_b d\tau .$$

(11)

Here, ψ_a and ψ_b denote the eigenfunctions $\sqrt{\dfrac{\epsilon^3}{\pi}}\, e^{-\epsilon r}{}_a$ and $\sqrt{\dfrac{\epsilon^3}{\pi}}\, e^{-\epsilon r}{}_b$, belong- <u>/932</u>

ing to the two atoms. The component W_0 represents the interaction that would take place on neglecting the auxiliary potential and the fact that ψ_a, ψ_b are no eigenfunctions of the unperturbed Hamiltonian function. The first expression in parentheses is the Coulomb interaction and the exchange of the two valence electrons under the influence of the auxiliary field. The second expression in parentheses is due to the fact that our initial function represents only an approximation but no true eigenfunction of the unperturbed atoms. Here, W_0 is the known function calculated by Sugiura for H_2; we merely have to multiply his energy values by ϵ and divide his distances by ϵ. The other integrals are easy to evaluate, for which the reader is referred to the Appendix.

Calculation of W as a function of the nuclear distance R yields a minimum at R = 4.0 Å of -0.19 v. The experimental values are R = 3.9 Å and W = -0.51 v. Whereas the distance is more or less correct, the energy in this approximation of the perturbation calculation is by far too low. The reason mainly lies in the auxiliary potential; W_0 alone, at the same distance, is $W_0 = -0.71$ v which means that it is even greater than the experimental value of the energy.

The equilibrium distance for W_0 alone would be 3.0 Å at an energy of -0.91 v. Using W_0 exclusively, approximately corresponds to elimination of all rumpf effects in the conventional perturbation calculus. As expected, the energy will then become much too low[*]. The finding that, in considering the rumpf effect, the obtained energy is much too low agrees excellently with the results obtained

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[*] See the discussion of earlier papers, in which an analogous calculation method was used by James (loc. cit.); see especially (Ref.7).

by M. James for Li_2 in his consequent consideration of the entire rumpf effect within the scope of a Heitler-London perturbation method. In this approximation, James obtained only 24 - 29% of the true energy. For the case of H_2, the corresponding percentage is 67%. Accordingly, it could be expected that this will decrease further for K_2; in fact, it would not be surprising if the Heitler-London calculus were to furnish positive energy values for K_2. The fact that our result, compared to the results by James, is still relatively /933 favorable is due in part to our neglecting the mutual interaction of the rumpfs or, in part, to a somewhat too favorable auxiliary function and to the fact that polarization forces between electrons and rumpf were included. We share James' opinion that the energy deficiency, in higher approximations especially on introducing the interelectron distance, will appear as the coordinate of a variational problem. Such an argument means that the electrons cannot be permitted to "revolve" independently of one another. It is exactly at low energies of the electrons that their mutual repulsion will keep them apart at all times and thus lead to a considerable diminution of the mean energy. In the case of H_2^-, this effect is about 1.5 v (Ref. 9). It is true that in the case of K_2, the two electrons are not compressed into a small space but their zero-point energy is less. It is entirely plausible to assume an effect of -0.3 v, due to mutual polarization. The justification of this assumption must be demonstrated by an exact calculation according to Ritz' method which should be carried out in approximately the manner used by James and Coolidge (Ref. 10) for the case of H_2. That the participation of ionic states and variations of ϵ produce only a negligible improvement in the energy can be estimated also in our case.

An especially surprising effect discovered by James was the decrease of the triplet term under the influence of the atom rumpf. However, this effect is obtained automatically in our method since any reduction in the amount of the exchange integral means a rise of the singlet and a drop of the triplet term. Since the contribution of the auxiliary potential to the exchange exceeds the corresponding diagonal term, the triplet term in our method is lower with an auxiliary field than without such a field. At 4 Å, we obtain a value of only +0.4 v with an auxiliary potential instead of a value of +0.9 v without such a potential. James reported that the closed shells influence the exchange integrals of the valence electrons only by the fact that permutations of the electrons higher than simple transpositions are considered here; otherwise, the rumpfs would enter only additively along with the Coulomb interaction. The fact that these higher exchange effects are covered by our Thomas-Fermi theory constitutes a strong substantiation for our attempted arguments.

7. The KH Molecule   /934

As a second example, let us consider the KH molecule. Here, it is necessary to have homopolar and ionic states participate in the binding. Despite the fact that the ionic molecule seems more plausible per se, atomic states may play a certain role in the binding. For LiH, Hutchisson and Muskat (Ref. 11) found a correct energy even under the assumption of pure atomic binding. However, for the calculation method used, the criticism voiced by us and also by James (loc. cit.) holds. Nevertheless, for the time being, both binding types will be allowed to participate in the KH molecule.

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The homopolar state has the eigenfunction $\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)$, where it is assumed that $\psi_a = \sqrt{\dfrac{\varepsilon^3}{\pi}}\, e^{-\varepsilon r_a}$, $\psi_b = \sqrt{\dfrac{1}{\pi}}\, e^{-r_b}$. The subscript b thus

characterizes the H atom. The ionic term is somewhat more difficult. The formula $\psi_b(1)\psi_b(2)$ for this term would constitute too poor an approximation. Similarly, even the formula $\psi_c(1)\psi_c(2)$ with a shielded H eigenfunction ψ_c would still be poor. It is known (Ref.9) that this formula, for the free H, furnishes an electron affinity of -0.74 v instead of the real +0.712 v. Without introducing the r_{12} coordinate, the result can be improved further if, for both electrons of H⁻, different eigenfunctions are used and if symmetrization is performed, i.e., if $\psi_c(1)\psi_d(2) + \psi_d(1)\psi_c(2)$ is used for the ionic state, where ψ_c and ψ_d are H eigenfunctions with differing degree of shielding. To prevent excessive complication of our estimate calculation, we assume the function

$\sqrt{\dfrac{\varepsilon^3}{\pi}}\, e^{-\varepsilon r_b}$ for ψ_c, i.e., the same function as for Li except that we calculate

here from the nucleus b and use the hydrogen function for ψ_d, i.e., $\psi_d = \psi_b$. This yields the increase in total atomic radius of H⁻ compared to H; the electron affinity of the free H⁻, using these functions, becomes +0.34 v and thus has considerably approached the real value +0.712 v.

Consequently, our total eigenfunction becomes

$$\psi = \psi_a(1)\,\psi_b(2) + \psi_b(1)\,\psi_a(2) + \sigma[\psi_b(1)\psi_c(2) + \psi_c(1)\,\psi_b(2)] \tag{12a}$$

where the coefficient σ must be conceived as a variational parameter and must be so determined that the total energy becomes a minimum.

This is obtained as

$$\overline{H} = \frac{P + 2\sigma Q + \sigma^2 R}{p + 2\sigma q + \sigma^2 r} \tag{12b}$$

where P, Q, R denote the following integrals:

$$\left.\begin{aligned}
P &= \int [\psi_a(1)\,\psi_b(2) + \psi_b(1)\,\psi_a(2)]\, H\psi_a(1)\,\psi_b(2)\, d\tau_1 d\tau_2 \\
Q &= \int [\psi_b(1)\,\psi_c(2) + \psi_c(1)\,\psi_b(2)]\, H\psi_a(1)\,\psi_b(2)\, d\tau_1 d\tau_2 \\
R &= \int [\psi_b(1)\,\psi_c(2) + \psi_c(1)\,\psi_b(2)]\, H\psi_b(1)\,\psi_c(2)\, d\tau_1 d\tau_2
\end{aligned}\right\} \cdot \tag{12c}$$

The small values p, q, r are obtained from the large values P, Q, R by setting

H = 1. Except for the integral $I = \int \dfrac{1}{r_{12}}\, \psi_a(1)\psi_b(1)\psi_a(2)\psi_b(2)\, d\tau_1 d\tau_2$ which is

contained in P, the integrals occurring here are entirely elementary and can be reduced to the simple type given in the Appendix. For the estimate of I, the reader is again referred to the Appendix.

As a result, we obtain an equilibrium distance of 2.1 Å with an energy of

-0.8 v. Here, the participation of the ionic state $\dfrac{\sigma^2}{1 + \sigma^2}$ is 80%. This in

itself would already give -0.7 v and the homopolar state alone would yield
-0.3 v. The experimental data are as follows: equilibrium distance = 2.2 Å;
dissociation energy: 2.06 v.

As in the case of K_2, we again obtained only a fraction of the experimental
energy. The reason is the same as before, since the coupling of the electron
motion (for example, measured by a term with r_{12} in the total eigenfunction) had
been disregarded both in the ionic state and in the homopolar state. However,
we must add here that our calculation employed rather arbitrary eigenfunctions
of the ionic state; in this case, the introduction and variation of shielding
parameters presumably would have led to considerable improvement. Despite the
unfavorable value of the total energy, we are inclined to consider as real the
observed strong participation of the ionic state in the binding.

The attempt at interpreting the KH molecule as a purely ionic molecule also
yields a verification for our statements that the main reason for the energy
deficiency is coupling of the electron motions. This is substantiated by the <u>/936</u>
fact that, for the pure ionic state, we can take the total interaction of the
two electrons from data furnished by other authors, for example by Bethe (Ref.9)
who calculated this interaction, in high approximation, for the free H^- accord-
ing to Hylleraas. In our subsequent perturbation calculus, we then no longer
use the eigenfunctions of the two electrons but only their total resultant
density distribution. For the latter, we set up another simplified formula,

namely $\rho = 2 \dfrac{\alpha^3}{\pi} e^{-2\alpha r} \cdot \alpha$. Here, α is given a value of 11/16, obtained by

placing both electrons in the same state and seeking the value α that makes the
total energy a minimum. The difference of this distribution from the real
density distribution can be read from the illustration given by Bethe (loc.
cit.). The maximum of the real density distribution is located somewhat farther
inside but for that drops in a somewhat more shallow manner toward the outside.
Presumably, our value of ρ will be quite useful as an approximate criterion for
the "atomic radius" of H^-.

Now, the calculation becomes quite simple. First, the regular Coulomb in-

teraction $a = -\dfrac{1}{R}$ of two monovalent ions at a distance R must be supplemented

by the known shielding effect due to the finite extent of the charge cloud of

the H^- electrons $b = 2\left(\dfrac{1}{r} + \alpha\right)e^{-2\alpha R}$. Secondly, this must be supplemented

further by the repulsion due to penetration of the H^- charges into the rumpf
of K^+:

$$c = 2\,\frac{\alpha^3}{\pi}\,A\int \frac{e^{-2\alpha r_a}}{r_a}\,e^{-2\alpha r_b}\,d\tau = 2e^{-2\alpha R}\,\frac{A\alpha^5}{x^2-\alpha^2}\left(1 - \frac{\alpha}{R(x^2-\alpha^2)}\right) +$$
$$+ \frac{2A\alpha^4}{R(x^2-\alpha^2)^2}\,e^{-2xR} \tag{13}$$

Finally, the known difference between ionization energy of the K atom and electron affinity of the H atom must be taken into consideration; this is d =
= 4.32 - 0.72 = 3.60 v.

Using all four components, an equilibrium distance of 1.9 Å (exp: 2.2 Å) and a dissociation energy of 1.95 v (exp: 2.06 v) are obtained. The agreement is rather satisfactory here; the fact that the distance is somewhat too small might be attributable to the excessively rapid drop of our ρ value at large /1937 distances. Under application of Bethe's density distribution, the atoms presumably are forced somewhat apart, and the resultant energy drop can be compensated again by the polarization forces which we had disregarded.

The value of 1.95 v is composed of the following individual components:
  a = -1/R = - 7.52 v;
  shielding: b = +0.37 v;
  K^+ rumpf (Pauli principle): c = +1.60 v;
  difference between ionization energy of K and electron affinity of H:
  d = +3.60 v.

It is obvious that the "ionic radius" of K, produced by the Pauli principle, plays a decisive role here. This calculation, at least qualitatively, also confirms our concept that the coupling between the motions of both electrons is of a major importance for the case of weak binding energies.

8. Conclusions

All above calculations are of a more or less orienting nature. However, according to the results obtained it seems useful to construct more precise formulas for solving the problems and to carry out the higher approximations, which are somewhat more cumbersome from the computational viewpoint. It can be hoped to settle activation questions with this method, without requiring an excessive number of arbitrary assumptions with respect to the interaction functions involved.

Available empirical data clearly indicate the direction in which the theory must proceed. Calculations along this line have been started at our Institute and will later be extended also to other atoms. We have in mind to apply the described approximation viewpoint to problems of polarizability of atoms and ions.

Summary: For an approximate treatment of the valence electrons of simple atoms, a modified Schrödinger equation is derived in which the total influence of the rumpf is taken into consideration by an auxiliary potential and in which the exclusion principle does not apply to the valence electrons. Basing the auxiliary potential on the Thomas-Fermi theory yields correct orders of mag- /1938 nitudes, while for practical application potential and eigenfunctions can be taken from the spectra.

Application to the binding energy of K_2, in the approximation of the Heitler-London perturbation method, furnishes only 37% of the real energy. Exactly this result is in excellent agreement with data obtained by James during

a consequent allowance for rumpf effects according to the Heitler–London method. For the case of KH, the same approximation yielded 39% of the real energy, at 80% participation of the ionic state. The main reason for the energy deficiency is the fact that the coupling of the orbital motions of the electrons, due to their interaction, had been neglected. In the limiting case of pure ionic binding, this value can be taken from the exact H^- theory, yielding a binding energy of 1.95 v (exp: 2.06 v) at a distance of 1.9 Å (exp: 2.2 Å). The calculations are being continued.

9. Mathematical Appendix

In addition to the elementary integrals which can be directly evaluated in spherical coordinates, two other types occur which are carried out in elliptic coordinates. We are noting these well-known integrals here:

$$\int \frac{e^{-ur_a}\, e^{-vr_b}}{r_a}\, d\tau =$$

$$= \frac{4\pi e^{-vR}}{u^2 - v^2}\left(1 - \frac{2v}{R(u^2 - v^2)}\right) + \frac{4\pi e^{-uR}}{u^2 - v^3}\frac{2v}{R(u^2 - v^2)} \tag{14}$$

$$\int e^{-ur_a}\, e^{-vr_b}\, d\tau =$$

$$= \frac{8\pi}{R(u^2 - v^2)^3}\left\{e^{-uR}[4uv + Rv(u^2 - v^2)] - e^{-vR}[4uv + Ru(v^2 - u^2)]\right\}.$$

To these, most integrals in which r_a and r_b occur, can be reduced. For example, we have

$$\int e^{-2\alpha r_{a1}}\frac{1}{r_{12}}\,\psi_a(2)\,\psi_b(2)\, d\tau_1 d\tau_2 =$$

$$= \frac{\pi}{\alpha^3}\int\left[\frac{1}{r_{a2}} - \left(\frac{1}{r_{a2}} + \alpha\right)e^{-2\alpha r_{a2}}\right]\psi_a(2)\,\psi_b(2)\, d\tau_2.$$

With ψ_a and ψ_b as exponential functions around the nucleus a resp. b, this will yield the above-given types of integrals. Difficulties are produced by only /939 one integral:

$$I = \frac{e^3}{\pi^3}\int\frac{1}{r_{12}}\,e^{-(ur_{a1} + r_{b1}) - (ur_{a2} + r_{b2})}\,d\tau_1 d\tau_2 .$$

The literature contains series expansions for this integral (Ref.12), but these are very cumbersome to handle especially if, as in our case, the convergence is poor. This leaves no other possibility than to break off the series arbitrarily after the first terms. For this reason, we prefer an entirely different method which seems useful for an estimation.

We base the process on the assumption that, for a large domain of R and ε,

the ratio of I to the sums of the analogous integrals, in which $\frac{1}{r_{12}}$ is replaced by $\frac{1}{r_{a1}}$ respectively by $\frac{1}{r_{b1}}$, remains relatively constant. To verify the justification of such an assumption, the ratio is calculated according to Sugiura in the first column of Table 1, for the limiting case $\epsilon = 1$. To estimate the manner in which this ratio varies with ϵ, let us consider the other limiting case $\epsilon \ll 1$ whose solution can also be given. The interatomic distance is assumed to be at least so large that the nucleus of the larger atom comes to lie entirely outside the smaller atom. Under the assumption $\epsilon \ll 1$, the charge distribution $e^{-\epsilon r_a - r_b}$ obviously becomes $e^{-\epsilon R_e - r_b}$ since, in the entire region in which the factor e^{-r_b} differs noticeably from zero, the other factor $e^{-\epsilon r_a}$ can be replaced by $e^{-\epsilon R}$. Integration yields $I = 20\epsilon^3 e^{-2\epsilon R}$. Under the mentioned assumptions, we obtain

$$\frac{\epsilon^3}{\pi^2} \int \left(\frac{1}{r_{a1}} + \frac{1}{r_{b1}} \right) e^{-(\epsilon r_{a1}' + r_{b1}) - (\epsilon r_{a2} + r_{b2})} d\tau_1 d\tau_2 = \left(\frac{64}{R} + 32 \right) \epsilon^3 e^{-2\epsilon R}.$$

Consequently, the sought ratio η will become $\eta = \frac{5}{8} \frac{R}{2 + R}$. This ratio is shown in column 2 of Table 1. It is obvious that the course with R is the same as at $\epsilon = 1$ and that even the absolute value for average R does not differ much from the value at $\epsilon = 1$. Finally, we interpolate linearly between $\epsilon = 0$ and $\epsilon = 1$, by conclusively writing

$$\eta = \frac{5}{8} \frac{R + \epsilon/2}{R + 2} \tag{15}$$

TABLE 1

R (a.u.)	η at $\epsilon = 1$ (strict)	$\frac{5}{8} \frac{R}{R+2}$	$\frac{5}{8} \frac{R+1/2}{R+2}$
2	0.39	0.31	0.39
3	0.42	0.38	0.44
4	0.46	0.42	0.47
5	0.48	0.45	0.49
6	0.50	0.47	0.51
10	0.56	0.52	0.55

As $\epsilon \to 0$ and at $R \gg 1$, the relation becomes strictly valid; for $\epsilon = 1$, column 3 of Table 1 shows that the approximation is satisfactory. On applying this formula to intermediate values of ϵ, the error most likely will not be more than a few percent. We used this estimate above for $R = 4$.

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